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Final Technical Report

Interpretation of Near and Vacuum Ultraviolet Band Spectra

Vanderbilt University

1 June, 1963 to 31 May, 1964

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K. Keith Innes

Acknowledgement

We are most grateful for ARPA support and believe that it has led directly to the best spectroscopic research at Vanderbilt so far. There is every reason to believe that work in the coming year will be still more fruitful.

Final Technical Report

I. Staff

The principal investigator lectured on work under this grant at the Naval Research Laboratory and the National Research Council of Canada in July, 1963 and to the Working Group on Thermochemistry in November, 1963. He organized a Symposium on Electronic Spectra for the Southeastern Meeting of the American Chemical Society in November, 1963 and will accompany Mr. C. W. Mathews to the Symposium on Molecular Spectroscopy and Structure at Columbus in June, 1964 for presentation of a paper on BF_3 discharges. He began a term on the Editorial Advisory Board of the Journal of Molecular Spectroscopy in May, 1964.

Dr. S. V. K. Rao returned to India in April, 1964.

Mr. C. W. Mathews will receive his Ph.D. degree during the summer of 1964 and will remain as postdoctoral associate under this grant for approximately one year. The other graduate student who worked under the grant this year was Mr. Paul C. Poynor.

Undergraduates who had summer research experience were W. Greer and H. McSwiney. Mr. Greer will be back this summer and will be joined by Mr. J. MacDonald.

Miss S. Cook has continued as Research Technician and Assistant.

II. Publications since May, 1963 are:

A. "The Band Spectrum of the InH Molecule: Characterization of the $^3\Pi$ State," J. Molecular Spectroscopy 11, 301(1963)

B. "Forbidden Character in the 3200A Transitions of Pyrazine-h_4 and -d_4 Vapors," J. Molecular Spectroscopy 11, 257(1963)

C. "Polarization and Assignment of the 3700A Absorption Spectrum of 1,4-Diazine Vapor," Disc. Faraday Society, (1963), No. 35, 192,237.

D. "Ultraviolet Spectroscopy," Proceedings of the First Meeting of the Working Group on Thermochemistry," Vol.I, 31(1963).

E. "The Band Spectrum of the Al_2 Molecule," Astrophys. J. 139, 365(1964)

F. "Identification of the 5450A Emission from Discharges Through BF_3 Vapor," in press, J. Molecular Spectroscopy.

Interpretation of Near and Vacuum Ultraviolet Band Spectra

I. The Spectrum of the BOF_2 Molecule.

Violet-degraded bands between 5600 and 6000A from a discharge through BF_3 vapor have been studied with the goal of positive identification of the emitter. The boron and oxygen vibrational isotope effects have shown that the emitting molecule contains only one each of these atoms. By studying the intensity of the bands as a function of the ratio of boron to fluorine the molecule has been found to contain two fluorine atoms. Silicon and hydrogen, the two most likely impurity atoms, have been eliminated from consideration in separate experiments. Thus the emitter must be the BOF_2 molecule or molecule-ion. Assuming the former, it is interesting that it contains thirty-one electrons since the only other polyatomic radical containing thirty-one electrons is NO_3, which exhibits a spectrum in the same region.

The active vibrations are very close to the in-plane vibrations of the ground state of the BF_3 molecule and are consistent with C_{2v} symmetry in both electronic states. Walsh had earlier predicted that a molecule containing thirty-one electrons should be planar in its ground-state and lowest-lying excited state.

It is interesting too that although the thermodynamics is not unfavorable to observation of BOF_2, mass spectroscopic experiments with B, O_2, F_2 systems have not detected BOF_2 peaks. They have detected $HBOF_2$ and it may be that the mass 64.8 peak was masked by that arising from $HB^{10}OF_2$.

In any event this seems to be the first report of an observation of the BOF_2 molecule.

II. Other Studies

The spectrum of the B-Cl molecule has been extended into the vacuum ultraviolet region and is being studied at high resolution.

Attempts to improve knowledge of the AlO, MgS and BS_2 molecules have not so far met with appreciable success.

The analysis of the very complex spectrum of the BO_2 molecule (discussed in earlier reports) is proceeding now on the more solid foundation of spectra of $B^{10}O_2$ and $B^{11}O_2^{18}$, obtained in connection with the study discussed under I.

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